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TOXIWASP: A Dynamic Model for Simulating the Transport and Fate of Toxic Chemicals in Water Bodies

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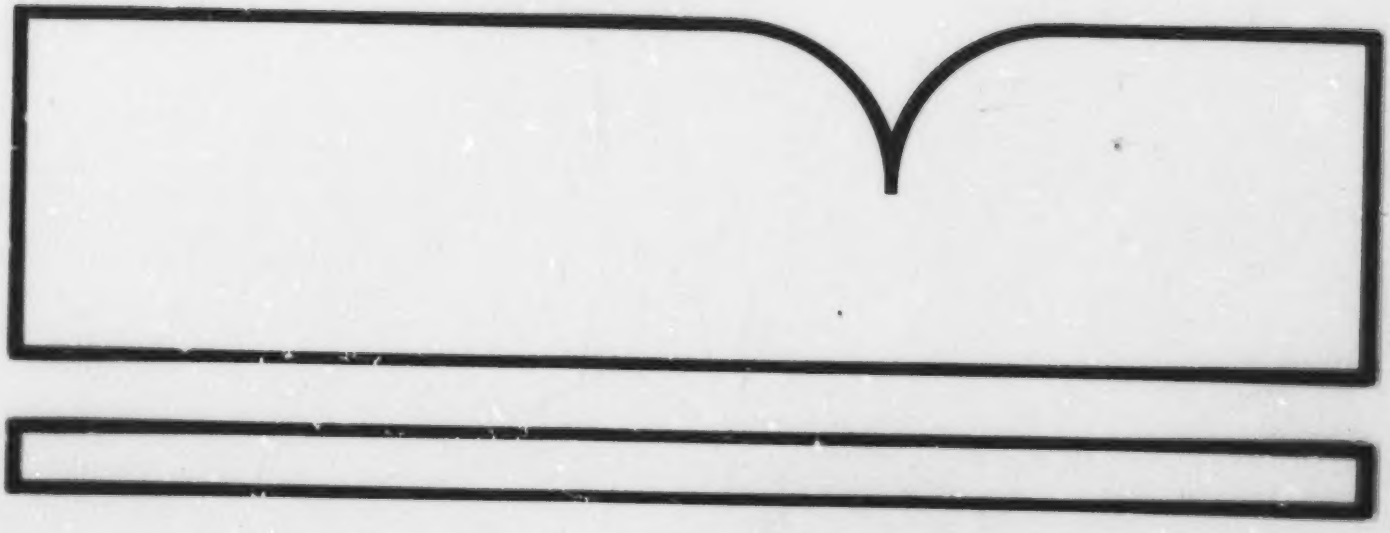

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TOXIWASP

by

Robert B. Ambrose, Jr.
Technology Development and Applications Branch
Environmental Research Laboratory
Athens, Georgia 30613

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16. ABSTRACT

TOXIWASP is a dynamic model for simulating the transport and fate of toxic chemicals in water bodies. Two state variables are simulated: organic chemical and total sediment. The generalized chemical model can be used for problems requiring dynamic transport and loading capabilities, simple mechanistic sediment predictions, and process-derived chemical predictions. TOXIWASP can be applied to stratified lakes and reservoirs, large rivers, estuaries, and coastal waters. Created for use in exposure assessments, the model allows the user to perform simple dynamic simulations of potentially toxic organic chemicals, such as pesticides. Dynamic simulations allow the consideration of variable loads, the prediction of peak events, and the estimation of time-varying chemical exposure.

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CHAPTER 7
TOXIWASP

7.1 BACKGROUND

TOXIWASP is a dynamic model for simulating the transport and fate of toxic chemicals in water bodies. Two state variables are simulated: organic chemical and total sediment. The initial version of TOXIWASP was created by adapting the kinetic structure of the EXposure Analysis Modeling System (EXAMS) (Burns et al., 1982) to the transport framework provided by the Water Analysis Simulation Program (WASP) (DiToro et al., 1981), and adding simple sediment balance algorithms along with special input and output software. For Version 2, TOXIWASP was expanded to accept unsteady flows and volumes from one of three hydrodynamic models: DYNHYD and DYNHYD2 (Feigner and Harris, 1970; Roesch et al., 1979) or SWFLOW (Huber et al., 1975). The result is a generalized chemical model that can be used for problems requiring dynamic transport and loading capabilities, simple mechanistic sediment predictions, and process-derived chemical predictions. TOXIWASP can be applied to stratified lakes and reservoirs, large rivers, estuaries, and coastal waters.

The main component of TOXIWASP is WASP, a dynamic compartmental modeling program for aquatic systems. Time-varying transport, including forcing and boundary processes, advection, dispersion, and mass loading, are represented in this program. Water quality processes are represented in a special kinetic subroutine that is either chosen from a library or written by the user. WASP is structured to permit easy substitution of kinetic subroutines into the overall package to meet specific user needs.

The kinetic component of TOXIWASP was modified from EXAMS. From chemical characteristics of a compound and the environmental parameters of an aquatic system, EXAMS formulates a total transformation rate. This rate is based on a simple addition of the pseudo-first order rate constants for each process. In TOXIWASP a kinetic derivative is calculated from this rate and passed to standard WASP subroutines, where it is integrated along with transport and loading derivatives to yield time-varying chemical concentrations for a specified spatial network.

The external hydrodynamic components of TOXIWASP Version 2 are link-node models, which represent rivers, bays, and estuaries as a series of junctions (or nodes) connected by a series of channels (or links). Junctions are characterized by their volumes, whereas channels are characterized by their flows. DYNHYD and DYNHYD2 are hydrodynamic submodels from the Dynamic Estuary Model (DEM). SWFLOW is the hydrodynamic submodel from RECEIV and the Stormwater Management Model (SWMM).

Bringing together modeling technology from WASP, EXAMS, and DYNHYD, then, TOXIWASP allows the user to perform simple dynamic simulations of potentially toxic organic chemicals, such as pesticides. Dynamic simulations allow the consideration of variable loads, the prediction of peak events, and the estimation of time-varying chemical exposure. TOXIWASP was created for use in exposure assessment.

7.2 USE OF TOXIWASP IN EXPOSURE ASSESSMENT

Evidence of potentially harmful effects of pesticides and other toxic organic chemicals on aquatic organisms has led to intensive efforts toward environmental risk assessment for existing and new chemicals. The concept of risk reflects the likelihood or probability of causing such effects. Obviously, if an effect is induced, the organism affected must first have been exposed to the toxicant for a time period and intensity sufficient to inflict the damage. The study of this exposure, or exposure assessment, is defined as a quantitative evaluation of the concentration of chemical toxicants in contact with receptor populations.

The source of toxic chemicals in a river basin is an important factor in selection of techniques to analyze the problem. Toxic chemical releases may arise from both nonpoint sources such as agricultural fields from which pesticides are transported in runoff, and point sources such as chemical manufacturing plants from which chemicals are discharged in effluents. Nonpoint sources are characterized by highly variable loadings with rainfall-runoff events dominating the timing and magnitude of chemical inputs to the receiving waters. Point sources are usually much less varied and are sometimes approximated as steady inputs to the aquatic system.

Chemical concentrations in aquatic environments also are determined by the transport and transformation processes that occur in river basins. As chemicals are transported by water or sediment, they are subject to a number of physical, chemical, and biological processes that can lead to either transport or transformation. The influence of transport on chemical behavior is determined by the local environmental regime (flow rates, sediment concentrations, etc.) and such chemical properties as the partition coefficient. Transformation processes are determined by chemical properties and by such environmental conditions as pH and temperature.

Exposure assessment as a part of risk evaluation implies the need to estimate probability of exposure. Exposure can be viewed as the realization of the joint probability of an ambient concentration and the existence of receptor populations. The probability of ambient concentrations can be approximated by calculating their frequency of occurrence over a sufficient period of time. A convenient way to represent frequency is the cumulative distribution function (cdf). A cdf can be expressed as a graph of the concentrations (on the abcissa) exceeded for various fractions of a time period (on the ordinate). A cdf can be related to average expected return periods for different concentrations. Given the cdf for a specific chemical in a specific environment, one can, for example, say that once every 10 years the concentration of a specific chemical will exceed a specified

level. The concentration level can then be related to biological effects information (e.g., LC_{50} values) and a return interval for damage (or risk) results. A cdf can be readily constructed given sufficient data in the form of time-series chemical concentrations. Rarely are any such data available, however, and when short time periods are sampled, the statistical reliability of the resulting data is always suspect. An alternative to field sampling is mathematical simulation with a dynamic model such as TOXIWASP.

If the user wishes, TOXIWASP can produce a time-series of chemical concentrations at a segment that reflects daily changes in flow and loading, and seasonal changes in water temperature, light intensity, wind speed, pH, and POH. TOXIWASP cannot simulate stochastic variability or variability below the resolution of its time step, which is usually between one and twelve hours. Nevertheless, the cdf constructed by TOXIWASP for a specified location reflects the probability of exposure of local receptor populations to a range of chemical concentrations. For populations that can avoid locally high chemical concentrations, the problem of estimating exposure is more difficult. The spatial variability of peak concentrations must be examined to estimate the probability of avoidance. While TOXIWASP can provide the spatial variability during peak concentration events, users must convert this information to their own estimates of avoidance.

7.3 OVERVIEW OF TOXIWASP CAPABILITIES

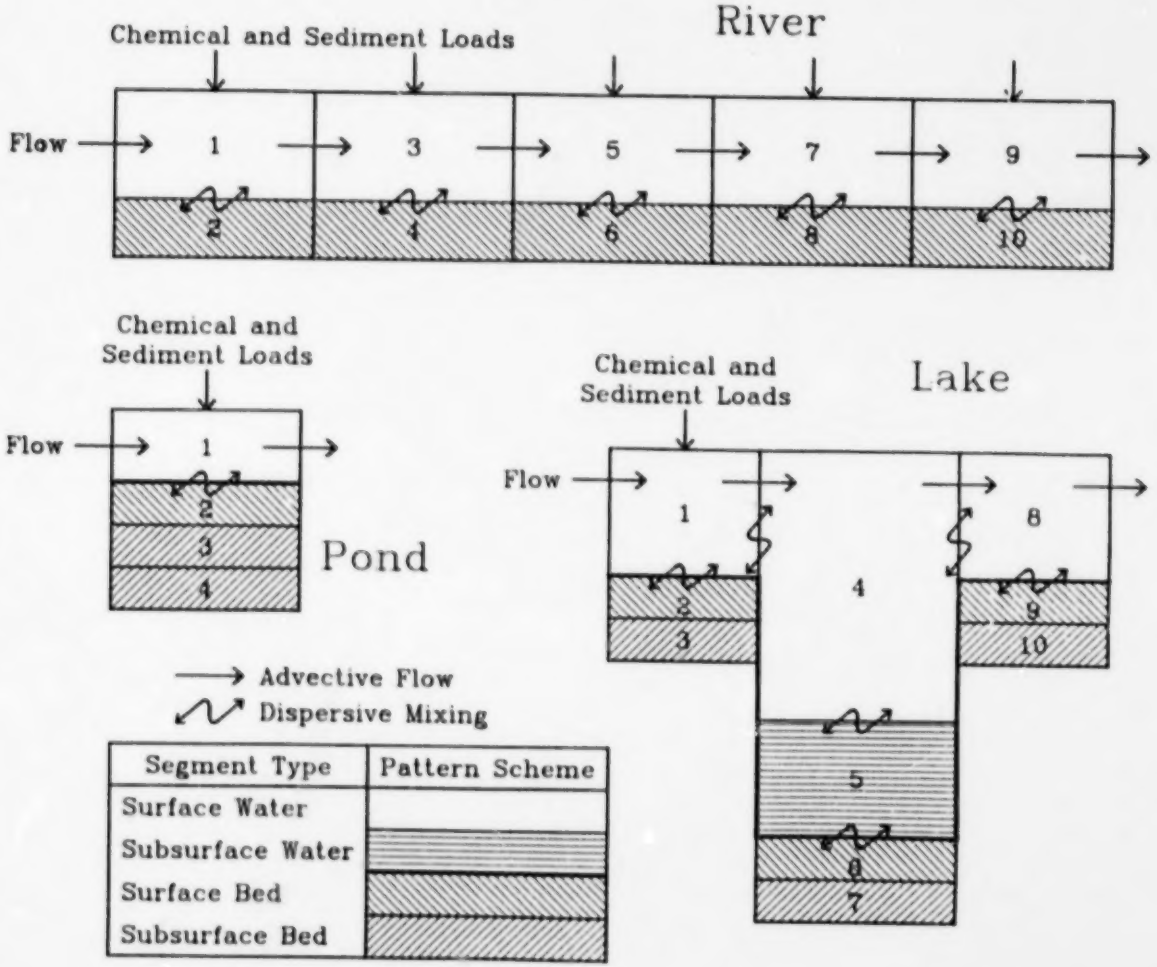
TOXIWASP uses the compartment modeling approach whereby segments can be arranged in a one-, two-, or three-dimensional configuration, as in Figure 7-1. Pollutant transport is based on user-specified flow and dispersive mixing between segments. All parameters and forcing functions may vary in space and time. TOXIWASP calculates time-varying water quality concentrations using an explicit, backward difference numerical solution to the mass flux form of the one dimensional advective-dispersive equation:

$$\frac{\Delta M_j}{\Delta t} = \sum_{i=1}^{n} [Q_{ij}C_i + E_{ij}A_{ij}(\frac{\Delta C}{L})_{ij}] + W_j - KV_j \qquad (1)$$

where M = constituent mass
C = constituent concentration, ML^{-3}
Q = water flow, L^3T^{-1}
E = longitudinal dispersion, L^2T^{-1}
A = cross-sectional area, L^2
L = characteristic mixing length, L
W = mass loading, MT^{-1}
K = kinetic degradation or transformation rate, $ML^{-3}T^{-1}$
V = segment volume, L^3
j = segment number
i = adjacent segments
ij = interface between segment j and adjacent segments i
n = number of segments i adjacent to segment j
t = time, T

Figure 7-1

Examples of TOXIWASP Network Configurations



TOXIWASP was created from WASP by adding a set of subroutines that calculate chemical degradation (the last term in equation 1) and that calculate special bed sediment transport processes such as sediment-water dispersive exchange, pore water percolation, and net burial-scour. The two differential equations solved by TOXIWASP for water-borne chemical and sediment, written in the general concentration form, are:

$$\frac{\partial C1}{\partial t} = -u\frac{\partial C1}{\partial x} + \frac{\partial}{\partial x}\left(E_x\frac{\partial C1}{\partial x}\right) + \frac{W1}{V} - K + \dot{S}_1 \qquad (2a)$$

$$\frac{\partial C2}{\partial t} = -u\frac{\partial C2}{\partial x} + \frac{\partial}{\partial x}\left(E\frac{\partial C2}{\partial x}\right) + \frac{W2}{V} + \dot{S}_2 \qquad (2b)$$

where C_1 = concentration of chemical, ML^{-3}
C_2 = concentration of suspended sediment, ML
u = flow velocity of water, LT^{-1}
W_1 = mass loading of chemical, MT^{-1}
W_2 = mass loading of sediment, MT^{-1}
$\dot{S}_1$ = net exchange of chemical with bed, $ML^{-3}\ T^{-1}$
$\dot{S}_2$ = net exchange of sediment with bed, $ML^{-3}\ T^{-1}$
x = longitudinal distance, L
t = time, T
M_s = mass of sediment

From chemical characteristics of a compound and the environmental parameters of the system, TOXIWASP formulates a total transformation rate. This rate is based on a simple addition of the pseudo-first order rates for hydrolysis, oxidation, biolysis, volatilization, and photolysis. Sorption onto sediments and onto biomass is calculated assuming local equilibrium, using a chemical-specific partition coefficient and spatially varying environmental organic carbon fractions.

TOXIWASP applies equations 2a and 2b, in the form of equation 1 to calculate sediment and chemical concentrations for every segment, including surface water, subsurface water, surface bed, and subsurface bed. Sediment is assumed to be a conservative constituent that is advected and dispersed among water segments and that can settle to and scour from bed segments.

In a simulation, the chemical undergoes first-order decay based on summation of several process rates, some of which are second-order. The effective first order decay rate can vary with time, then, and is recalculated as often as necessary throughout a simulation. The chemical is advected and dispersed among water segments and can be transported to the bed by sorption onto sediment and subsequent settling, or by dispersive mixing between the top bed layer and the bottom water layer. Within the bed, the chemical can migrate downward or upward through percolation and pore water diffusion. No lateral migration of the chemical within the bed is allowed.

Because the kinetic transformation processes are all expressed in terms of first-order rates, large loadings may cause problems by changing the characteristics of the systems. For example, a chemical subject to alkaline hydrolysis may kill the biological component, making the system less alkaline,

and thus reducing the alkaline hydrolysis degradation rate. The user must anticipate these problems and look for cases where they might happen. The task of keeping track of all possible ecosystem variables is too complex, and would occupy too much computer space for TOXIWASP. Therefore, feedback phenomena are not considered.

TOXIWASP is based on the following assumptions.

1. All segments are well mixed.
2. Sorption is an essentially instantaneous process within each segment (thus local equilibrium).
3. Chemical properties of the compound can be coupled with the characteristics of the environment to formulate a pseudo-first-order rate for each of the degradation processes using primarily mechanistic equations.
4. Pseudo-first-order rates combine linearly to form a total degradation rate for the chemical toxicant in each segment.

In the following development it is convenient to define concentration related symbols as in Table 7-1.

7.4 SEDIMENT TRANSPORT PROCESSES

Sediment transport is an important process in hydraulics and river mechanics, but its role in pollutant transport is not fully known. Several investigators (Karickhoff et al., 1979; Rao and Davidson, 1980) have shown that for most organic toxicants, particularly non-polar compounds, the sediment organic matter determines the extent of sorption and hence the importance of sorbed-pollutant transport. The particle size of the sediments is influential, but Rao and Davidson (1980) have shown that the organic matter content of each size fraction is the controlling factor. Organic matter content and surface area relationships suggest that silt and clay size sediment fractions are most relevant in sediment transport. One outcome of this rationale is the idea that, in river systems, wash load or suspended sediment is the important pollutant transport medium rather than bed load. If bed load transport can be ignored, the problem remains to estimate suspended sediment.

TOXIWASP treats sediment as a single size fraction that is advected and dispersed in the water and that settles (and deposits) at a constant, spatially variable velocity. Sediment is returned from the bed to the water column through a spatially variable scour (or erosion) velocity. Thus the net exchange of sediment with the bed, S_2 in Equation 2b, is calculated as

$$S_2 = \frac{W_s S_b}{L_b} - \frac{W_d S_w}{L_w} \qquad (3)$$

where W_s = scour (erosion) velocity of bed sediment, LT^{-1}
W_d = deposition velocity of suspended sediment, LT^{-1}
L_b = depth of active bed sediment layer, L
L_w = depth of water layer, L
S_b = concentration of sediment in bed, ML^{-3}
S_w = concentration of sediment in water, ML^{-3}

Table 7.1. Concentration Related Symbols
Used in Mathematical Equations

Symbol	Definition	Units*
C, C_1	Concentration of chemical (bed or water)	mgc/l_T
C_w	Concentration of dissolved chemical in water	mgc/l_T
C_w'	Concentration of dissolved chemical in water, $C_w' = C_w/\emptyset$	mgc/l_w
C_s	Concentration of sorbed chemical in water	mgc/l_T
C_s'	Concentration of sorbed chemical in water, $C_s' = C_s/S_w$	mgc/kgs
C_p	Concentration of dissolved chemical in bed (pore water)	mgc/l_T
C_p'	Concentration of dissolved chemical in bed (pore water), $C_p' = C_p/\emptyset$	mgc/l_w
C_b	Concentration of sorbed chemical in bed	mgc/l_T
C_b'	Concentration of sorbed chemical in bed, $C_b' = C_b/S_b$	mgc/kgs
C_2	Concentration of sediment (bed or water)	mgs/l_T
S	Concentration of sediment (bed or water), $S = C_2 * 10^{-6}$	kgs/l_T
S'	Concentration of sediment (bed or water), $S' = S/\emptyset$	kgs/l_w
S_w	Concentration of sediment in water	kgs/l_T
S_b	Concentration of sediment in bed	kgs/l_T
$\emptyset$	Porosity or volume water per volume segment	l_w/l_T
*	Partition coefficient of chemical on sediment	l_w/kgs

*mgc = milligrams of chemical
l_T = liters total volume of environmental segment
l_w = liters of water in environmental segment
kgs = kilograms of sediment (dry weight)

Nonzero values for $\dot{S}_2$ will lead to net sedimentation or erosion.

Sediment transport processes are illustrated in Figure 7-2.

7.5 CHEMICAL PARTITIONING (SORPTION) PROCESSES

The interaction of dissolved organic toxicants with entrained sediment is an important process that must be accounted for mathematically. If one assumes sorption is kinetically a first order process, then a rate equation similar to the other expressions can be written as:

$$\frac{R_S}{S} = k_s C'_w - k_d C'_s \tag{4}$$

where R_S = net rate of chemical transfer between dissolved and sorbed state, $ML^{-3}T^{-1}$ (typically mgc/l_T-hour)
k_s = rate constant for sorption, $L^3M^{-1}T^{-1}$ (typically l_w/kgs-hour)
k_d = rate constant for desorption, T^{-1} (typically per hour)

If one assumes $R_S = 0$ then

$$k_s C'_w = k_d C'_s$$

or
$$C'_s = \frac{k_s}{k_d} C'_w \tag{5}$$

Note that equation 5 is the linear form of the Freundlich isotherm with the ratio k_s/k_d being the distribution (or partition) coefficient (sometimes denoted as "π"). This coefficient is a function of characteristics of both the toxicant and the sediments onto which sorption has occurred. Many organic pollutants of current interest are non-polar, hydrophobic compounds whose π values correlate quite well with the organic fraction of the sediment. Rao and Davidson (1980) and Karickhoff et al. (1979) have developed empirical expressions relating equilibrium coefficients to laboratory measurements leading to fairly reliable means of estimating appropriate values.

TOXIWASP assumes that sorption is essentially instantaneous and considers it to be an equilibrium process. The model allows for three sorption possibilities--1. dissolved, 2. sediment sorbed, and 3. biota sorbed. The corresponding fractions of the chemical in each form, ALPHA(1), ALPHA(2), and ALPHA(3), are calculated for each compartment based on 12 segment parameters, constants, and state variables:

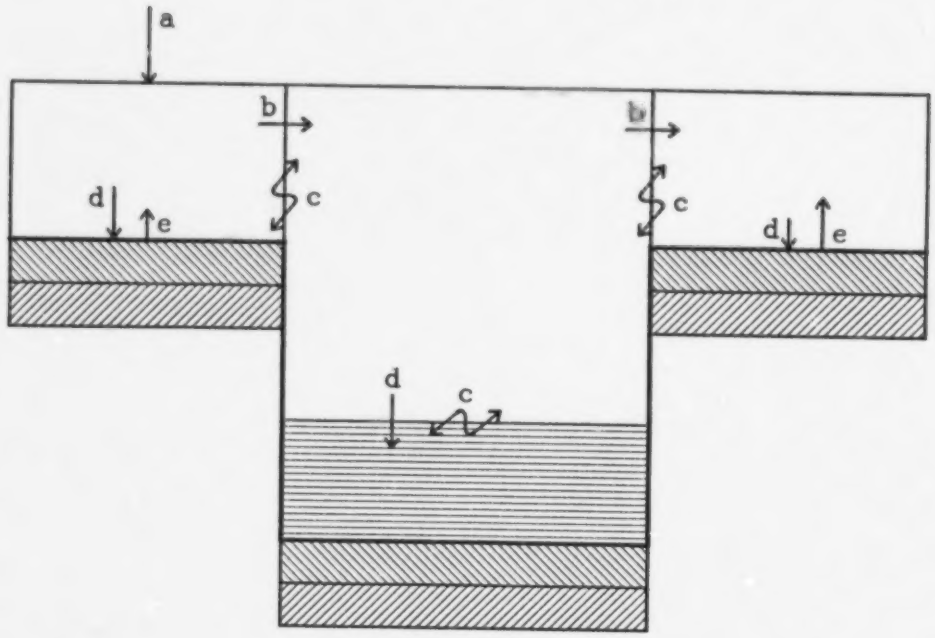
$$\text{ALPHA(1)} = \frac{1}{1 + KP * S/FRW + KB * B/FRW} = \alpha_1 \tag{6}$$

$$\text{ALPHA(2)} = \frac{KP * S/FRW}{1 + KP * S/FRW + KB * B/FRW} = \alpha_2 \tag{7}$$

$$\text{ALPHA(3)} = \frac{KB * B/FRW}{1 + KP * S/FRW + KB * B/FRW} = \alpha_3 \tag{8}$$

Figure 7-2

TOXIWASP Sediment Transport Processes



Process	Segment Types
a) Mass Loading	1,2 to Water
b) Advection	1,2 Water-Water
c) Dispersion	1,2 Water-Water
d) Settling	1,2 Water-Water or Water-Bed
e) Erosion	3 Surface Bed-Water

where KP = partition coefficient of the chemical on the sediment (l_w/kgs) = KOC * OCS(J) = π
KB = partition coefficient of the chemical with biota (l_w/kgb) = KOC * OCB
S = concentration of sediment, kgs/l_T
B = concentration of biomass, kgb/l_T
FRW = porosity of segment (water volume/total volume) = $\emptyset$

Based on the definitions for ALPHA, the following relationships hold:

$$\text{CHEM1} = \text{CHEM*ALPHA(1)} = C * \alpha_1 \quad (9)$$
$$\text{CHEM2} = \text{CHEM*ALPHA(2)} = C * \alpha_2 \quad (10)$$
$$\text{CHEM3} = \text{CHEM*ALPHA(3)} = C * \alpha_3 \quad (11)$$
$$\text{CHEM} = \text{CHEM1} + \text{CHEM2} + \text{CHEM3} = C(\alpha_1 + \alpha_2 + \alpha_3) \quad (12)$$

where CHEM = total chemical concentration in segment, mgc/l_T
CHEM1 = chemical dissolved in water phase of segment, mgc/l_T
CHEM2 = chemical sorbed onto sediment phase of segment, mgc/l_T
CHEM3 = chemical sorbed onto biological phase of segment, mgc/l_T

CHEM1, CHEM2, and CHEM3 are transformed into the following more common units for reporting:

$$\text{CHEMW} = \text{CHEM1/FRW} = C * \alpha_1/\emptyset \quad (13)$$
$$\text{CHEMS} = \text{CHEM2/S} = C * \alpha_2/S \quad (14)$$
$$\text{CHEMB} = \text{CHEM3/B} = C * \alpha_3/B \quad (15)$$

where CHEMW = chemical dissolved in water phase of segment, mgc/l_w
CHEMS = chemical sorbed onto sediment phase of segment, mgc/kgs
CHEMB = chemical sorbed onto biological phase of segment, ugc/$g_{biomass}$ (same as mgc/kgb)

7.6 BED-WATER CHEMICAL REDISTRIBUTION PROCESSES

An important, but poorly quantified, set of processes governs chemical exchange between the bed and the water column. A chemical may sorb onto suspended sediments and settle to the bed, or sorb directly to the bed surface when water concentrations are high. When water concentrations are low, the chemical may desorb from the bed surface. Turnover of the bed surface due to physical or biological processes should accelerate this sorption-desorption process. Diffusion of pore water into overlying water will also exchange dissolved chemicals. Percolation of pore water will move dissolved chemical up through the bed into the water column; infiltration can leach chemical down through the bed.

So even though bed load transport <u>per se</u> may be relatively unimportant in pollutant transport, interaction between the stream bed and the overlying water should not be ignored. Concentration gradients between the bed material and the overlying water will result in sorption and desorption and thus the stream bed can act either as a sink or a source of contaminants. For the stream bed one can write the dissolved and particulate chemical conservation equations:

$$\frac{\partial C_p}{\partial t} = \frac{\partial}{\partial y}\left(D^b \frac{\partial C_p}{\partial y}\right) - \frac{\partial (U_p C_p)}{\partial y} - R_s - K \qquad (16a)$$

$$\frac{\partial C_b}{\partial t} = \frac{\partial}{\partial y}\left(D^{bs} \frac{\partial C_b}{\partial y}\right) - \frac{W_s C_b}{L_s} + \frac{W_d C_s}{L_w} + R_s - K \qquad (16b)$$

where D^b = vertical dispersion coefficient for dissolved chemical, L^2T^{-1}
D^{bs} = vertical dispersion coefficient for sorbed chemical, L^2T^{-1}
U_p = velocity of net pore water movement into or out of the bed, LT^{-1}
W_d, W_s = deposition and scour velocity of sediment between bed and water column, LT^{-1}
L_w = depth of water compartment, L
L_s = depth of active bed layer, L
y = vertical distance, L

Equation 16a accounts for diffusion-dispersion and pore water transport of pollutants between the bed and the overlying water column. Equation 16b accounts for sediment-bound transport by including the scour and deposition terms, W_s and W_d. Estimation usually requires a rigorous treatment of hydrodynamic forces and characterization of sediments (e.g., cohesiveness). Several approaches are available for this purpose, but many chemical exposure models either omit these processes entirely or lump them into an overall calibrated dispersion or exchange coefficient.

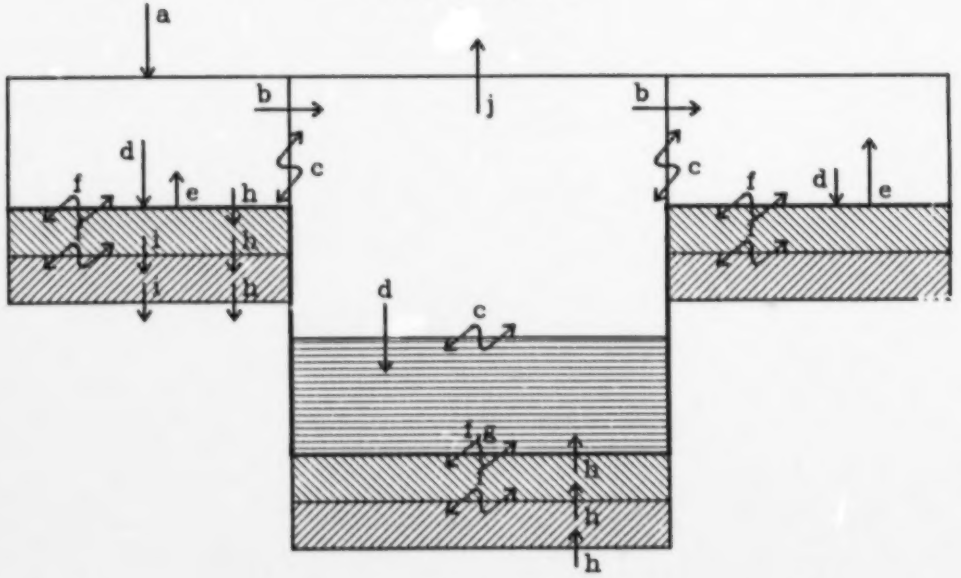
Comparing equations 16a and 16b with equation 2a reveals that $\dot{S}_1$, the net exchange of chemical from the bed to the water column, is a summation of several processes. These include pore water diffusion and percolation, bed sediment dispersion (due to physical mixing and bioturbation), scour and deposition, and direct sorption-desorption.

TOXIWASP handles the redistribution terms in equations 2a, 2b, 16a, and 16b as illustrated in Figure 7-3. The settling velocity W_d in equations 2a and 16b is a spatially variable parameter for suspended sediment and sorbed chemical. The scour velocity W_s in equation 16b is a spatially variable parameter for bed sediment and sorbed chemical. The pore water velocity U_p in equation 16a is another spatially variable parameter.

Another fundamental redistribution process in equation 16a is pore water diffusion. Its rate is controlled by the vertical concentration gradient and the vertical diffusion coefficient D^b. When processes other than molecular diffusion are acting in the bed, D^b is interpreted as a dispersion coefficient, and its value is higher. The vertical dispersion of sorbed chemical is represented by D^{bs} in equation 16b. TOXIWASP reads D^b as the spatially variable dispersion parameter E(I). D^{bs} is related to D^b through the spatially variable multiplier DSPSED(J). Where only pore water diffusion is active, DSPSED(J) is set equal to 0. In actively mixed areas, DSPSED(J) is equal to 1.

Because these processes are poorly quantified and variable in space and time, most chemical models now take a largely empirical approach to sediment-water exchange.

Figure 7-3
TOXIWASP Chemical Transport and Redistribution Processes



Process	Segment Types
a) Mass Loading	1,2 to Water
b) Advection	1,2 Water-Water
c) Dispersion	1,2 Water-Water
d) Settling	1,2 Water-Water or Water-Bed
e) Erosion	3 Surface Bed-Water
f) Pore Water Diffusion	3,4 Surface Bed-Water or Bed-Bed
g) Sediment Turnover	3 Surface Bed-Water
h) Percolation	4 Bed-Bed or Bed-Water
i) Sedimentation	4 Bed-Bed
j) Volatilization	1 Surface Water

7.7 BED SEDIMENTATION AND EROSION

The chemical redistribution processes in Equations 16 and 17 and Figure 7-3 operate in reference to a fixed bed. When sediment deposition ($W_d S_w / L_w$) exceeds sediment scour ($W_s S_b / L_s$), however, net deposition can lead to a rising bed surface and burial of sorbed chemical. When sediment scour exceeds sediment deposition, net erosion can lead to a falling bed surface and release of previously buried sorbed chemical. In this section, the term "sedimentation" will refer to net sedimentation or erosion.

A simple method for treating sedimentation is to define bed segment locations in reference to the rising or falling bed surface. If the bed surface rises at W cm per year, then buried chemical descends through the bed at W cm per year in reference to the rising bed segments (all other bed dispersion processes being ignored for the moment). There are two complications in this approach. First, if the density of the bed increases with depth, then compression must be occuring, decreasing W and squeezing the pore water and dissolved chemical upward. Second, the simulation time step is extremely short in relation to the net sedimentation velocity. This leads to rather severe "numerical dispersion," a form of computational inaccuracy within the bed.

To handle the first complication, TOXIWASP assumes two types of bed sediment: an upper uncompacted layer with bulk density S_b, and lower, compacted layers with bulk density S_ℓ. Assuming that sedimentation is in equilibrium with net deposition, all bed properties remain constant. The sediment mass addition is:

$$\dot{M} = \left(\frac{W_d S_w}{L_w} - \frac{W_s S_b}{L_s} \right) V_s \qquad (17)$$

where $\dot{M}$ = sediment mass added to bed, MT^{-1}
V_s = volume of the upper layer, L^3, equal to $A_s L_s$
A_s = sediment surface area, L^2

The volume of sediment added to the upper layer is M/S_b, whereas the volume added to the lower layer is M/S. The difference in volumes is equal to the pore water volume squeezed out through compaction. The rise in the bed surface equals the volume added to the lower layer divided by the surface area:

$$W = \frac{\dot{M}}{A_s S_\ell} = W_d \frac{L_s}{L_w} \frac{S_w}{S_\ell} - W_s \frac{S_b}{S_\ell} \qquad (18)$$

The amount of chemical lost from the upper bed layer due to sedimentation is:

$$V_s \frac{\partial C}{\partial t} = -W A_s S_\ell \, C_b' - W A_s \left(\frac{S_\ell}{S_b} - 1 \right) C_p' \qquad (19)$$

where the first term represents sorbed chemical buried downward and the second term represents dissolved chemical squeezed upward.

TOXIWASP implements a version of this simple approach that amounts to a Lagrangian scheme for treating movement of chemical through the bed due to

sedimentation. The time step for sedimentation is calculated internally, based on the scour and deposition rates. Whereas the simulation time step is on the order of hours, the sedimentation time step is on the order of months to years. The sedimentation time step varies with location and time and is tailored to minimize numerical dispersion in sedimentation calculations.

If lower bed segments are not included in a TOXIWASP network, then chemical burial will not take place. The upper bed layer will increase in volume and depth with settling, or decrease in volume and depth with scour. TOXIWASP prevents both complete filling of the water column and complete erosion of the bed.

7.8 TRANSFORMATION PROCESSES

The rate equation for the transformation term K in equations 1, 2a, 16a, and 16b cannot be specified in a general form. Depending on the process under consideration, many variables may be influencing the rate, leading to a multi-term and often non-linear relationship. The problem becomes tractible, however, when it is assumed that the rates are first order with respect to the pollutant concentration for given environmental conditions, leading to

$$K = \sum_{j=1}^{n} k_j C \qquad (20)$$

where K = total transformation rate, ML-3T-1
k_j = pseudo-first order rate constant for the jth process, which can vary in space and time, T-1
n = number of processes operating on chemical

This first-order assumption is generally accepted to be accurate for most chemicals at environmental concentrations. The assumption is invalid at concentrations near the solubility limit, however. EXAMS does not allow simulations where predicted chemical concentrations exceed one half of the solubility limit. TOXIWASP does not automatically abort such runs. If the user sets CMAX(1) in Card Group K to zero, however, TOXIWASP will abort the simulation if concentrations become high enough to violate the first-order assumption. This is accomplished by setting CMAX(1) to one half of the solubility or 10-5 M, whichever is less. In any case, the user should analyze results and consider whether this and other assumptions are valid.

Only rarely does the simple mathematical form of equation 20 provide a rigorous description of the kinetics of pollutant degradation in aquatic systems. But if the influencing variables that lead to more complex expressions are reasonably constant for a specific situation then the influence can be lumped into the single value, k_j. The problem of calculating kinetic transformation then becomes one of calculating the rate constants k_j from chemical properties and environmental characteristics.

Several investigators have reported processes that influence pesticides (Mackay and Leinonen, 1975; Paris et al., 1975; Wolf et al., 1975; Wolf et al., 1977; Zepp et al., 1975). Smith et al. (1977) have identified the major

pathways that lead to transformation of organic pollutants in the aquatic environment. The role of these processes is receiving increasing attention and laboratory protocols for related measurements have been developed (Mill et al., 1982). The general processes identified include hydrolysis, photolysis, oxidation, microbial degradation, and volatilization. TOXIWASP calculates the individual rate constants k_j for each of these processes. Theory and assumptions are summarized below.

7.8.1 Hydrolysis

Hydrolysis, or reaction of the chemical with water, is known to be a major pathway for degradation of many toxic organics. Because hydrolysis can be influenced by pH, the appropriate rate constant, k_h, is written as

$$k_h = k_a[H^+] + k_n + k_b[OH^-] \qquad (21)$$

where k_h = net hydrolysis rate constant, T^{-1}
k_a, k_b = specific acid and base catalyzed rate constants, respectively, $L^{3n-1}T^{-1}$
k_n = neutral rate constant, T^{-1}

Estimates for k_a, k_b, and k_n can be determined from laboratory studies completed over a range of pH values (Mill et al., 1982). The remaining unknowns in equation 21 can be determined from pH measurements taken in the aquatic system under investigation or from data from simulations.

7.8.2 Photolysis

Photolysis rate constants are dependent upon both intensity of solar radiation and structure of the compound (Smith et al., 1977; Zepp and Cline, 1977). TOXIWASP calculates photolysis for water compartments using an average first order rate constant measured for near surface waters during cloudless conditions:

$$k_p = k_{pl}\,[L] \sum_{i=1}^{3} \phi_{pi}\,\alpha_i \qquad (22)$$

where k_{pl} = average first-order photolytic rate constant for water surface during cloudless conditions in summer, day-1
ϕ_{pi} = average reaction quantum yield for compound in form "i" (dissolved, sorbed, biosorbed), moles per einstein
[L] = fraction of cloudless summer surface light intensity in segment, unitless:

$$= \left(\frac{1-e^{-K_e \ell\, D_f}}{K_e \ell\, D_f}\right) * (1 - 0.056\ \text{CLOUDG}) * \text{FACTOR} * \text{LIGHTN}$$

K_e = segment light extinction coefficient, per meter
D_f = ratio of optical path length to vertical depth
CLOUDG = average cloud cover, tenths
0.056 = cloud type reduction factor (altostratus to altocumulus)
FACTOR = latitude correction factor

LIGHTN = normalized time function for light, representing diurnal or seasonal changes (0-1.0)

At the heart of this photolysis methodology are two principles. First, the intensity of light in the water column decreases exponentially as a function of depth according to the Beer-Lambert Law. The second principle involves "reaction quantum yields," the efficiency of the reactions in the pollutant due to absorption of electromagnetic radiation. The "reaction quantum yield" is actually one of several such yields. Although a molecule activated by light can undergo several transformations, we are solely interested in the disappearance yield, that is, the change from parent compound to daughter compounds.

7.8.3 Oxidation

In aquatic systems, chemical oxidation of organic toxicants can be a consequence of interactions between free radicals and the pollutants. Free radicals can be formed as a result of photochemical reactions. Free radicals that have received some attention in the literature include alkylperoxy radicals, $RO_2.$; OH radicals; and singlet oxygen. The oxidation process is modeled as a second order process:

$$R_{ox} = k_{ox} [RO_2.] \cdot C \qquad (23)$$

where R_{ox} = net oxidation rate, $ML^{-3}T^{-1}$
$[RO_2.]$ = molar concentration of oxidant, nL^{-3}
k_{ox} = second order oxidation rate constant, $L^{3}n^{-1}T^{-1}$

It should be noted that chemical oxidation is a result of a number of sequential and competing reactions.

Because of the large number of alkylperoxy radicals that potentially exist in the environment, it would be impossible to obtain estimates of k_{ox} for each species. Mill et al. (1982) propose estimation of a rate coefficient using t-butyl hydroperoxide as a model oxidizing agent. They argue that other alkylperoxides exhibit similar reactivities to within an order of magnitude.

In addition to estimating a rate coefficient, an estimate of free radical concentrations must be made to completely define the expression for free radical oxidation. Mill et al. (1982) report RO_2 concentrations on the order of 10^{-9} M and OH concentrations on the order of 10^{-17} M for a limited number of water bodies. Zepp et al. (1977) report an average value on the order of 10^{-12} M for singlet oxygen in water bodies sampled. The source of free radicals in natural waters is photolysis of naturally occurring organic molecules. If a water body is turbid or very deep, free radicals are likely to be generated only near the air-water interface, and consequently, chemical oxidation will be relatively less important. In such cases, the concentrations cited above are appropriate in only the near-surface zones of water bodies.

7.8.4 Microbial Degradation or Biolysis

Rate expressions for microbial degradation in aquatic systems must account for the concentration of microbes present, i.e., a second-order rate expression usually written as

$$R_{bac} = k_{bac} C_{bac} C \tag{24}$$

where R_{bac} = net microbial degradation rate, $ML^{-3}T^{-1}$
k_{bac} = second-order bacterial rate constant, $L^{-3}M^{-1}T^{-1}$
C_{bac} = concentration of the bacteria, ML^{-3}

The use of k_{bac} as defined in equation (24) follows from the Michaelis-Menten equation as follows.

$$\mu = \mu_{max} \frac{C}{K_m + C} \tag{25}$$

where μ = specific bacterial growth rate, T^{-1}
μ_{max} = maximum specific bacterial growth rate, T^{-1}
K_m = half saturation constant, ML^{-3}

Bacterial growth is related to chemical substrate degradation with the yield coefficient Y:

$$R_{bac} = \frac{1}{Y} \mu C_{bac} \tag{26}$$

where Y = yield coefficient, mass biomass produced per mass of chemical degraded

If $K_m >> C$ (usually the case at environmentally observed concentrations) then we can define k_{bac} as

$$k_{bac} = \frac{\mu max}{Y K_m} \tag{27}$$

and equation 24 results. Practical utilization of equations 24-27 is fraught with uncertainties and often one is left with the problem of estimating $k_{bac}C_{bac}$ as a single value for the system under investigation.

7.8.5 Volatilization

Another process that removes organic pollutants from the aquatic system is volatilization. Volatilization is not a transformation process *per se* because the mass of the parent compound is preserved but it can be lumped into the transformation terms. Volatilization is usually modeled as

$$R_v = k_v \left(C_w - \frac{C_g}{H}\right) \tag{28}$$

where R_v = net volatilization transfer rate, $ML^{-3}T^{-1}$
H = Henry's law constant
C_g = concentration of the chemical in the bulk gas phase, ML^{-3}

k_v = mass transfer coefficient divided by the average depth of the water body, T-1

In most cases, the concentrations of organic toxicants in the atmosphere are much lower than the partial pressures equilibrated with the organic concentration in water. Consequently, equation 28 can be approximated by

$$R_v = k_v C_w \tag{29}$$

The value of k_v, the mass transfer coefficient, depends on the intensity of turbulence in a water body and in the overlying atmosphere. Mackay and Leinonen (1975) have discussed conditions under which the value of k_v is primarily determined by the intensity of turbulence in the water. As the Henry's law coefficient increases, the mass transfer coefficient tends to be increasingly influenced by the intensity of turbulence in water. As the Henry's law coefficient decreases, the value of the mass transfer coefficient tends to be increasingly influenced by the intensity of atmospheric turbulence.

In TOXIWASP, the volatilization calculation is based on the two-resistance principle, with the rate constant k_v calculated as follows.

$$k_v = \frac{1/L_w}{RESLIQ + RESGAS} \tag{30}$$

$$RESLIQ = \frac{1}{KO2L * KVOG} \quad \text{or} \quad \frac{1}{KO2L \ / 32/MWTG} \tag{31a}$$

$$RESGAS = \frac{1}{H * WAT \ / 18/MWTG} \tag{31b}$$

$$\overline{TKEL * 8.206E\text{-}5}$$

KO2L = reaeration velocity in segment, meters per hour
KVOG = measured liquid phase transport resistance, ratio
MWTG = molecular weight of compound
WAT = piston velocity of water vapor, meters per second
= 0.1857 + 11.36 * WIND
WIND = local, time varying wind speed, meters per second
TKEL = water temperature, degrees Kelvin
8.206E-5 = gas constant

TOXIWASP calculates flow-induced reaeration based on the Covar method (Covar, 1976). This method calculates reaeration as a function of velocity and depth by one of three formulas--Owens, Churchill, or O'Connor-Dobbins, respectively:

K20 = 27.6*AVVELE0.67/AVDEPE0.85 (32a)
K20 = 14.8*AVVELE0.969/AVDEPE0.673 (32b)
or K20 = 16.4*AVVELE0.5/AVDEPE0.5 (32c)

where K20 = reaeration velocity at 20°C, cm/hr
AVVELE = average segment velocity, ft/sec
AVDEPE = average segment depth, ft

The Owens formula is automatically selected for segments with depth less than 2 feet. For segments deeper than 2 feet, the O'Connor-Dobbins or Churchill formula is selected based on a function of depth and velocity. Deeper, slowly moving rivers select O'Connor-Dobbins, while moderately shallow, faster moving streams select Churchill.

Whenever the volatilization rate is calculated during a simulation, wind-induced reaeration is determined by

$$K20 = -0.46 * WINDSG + 0.136 * WINDSG^2 \quad (33)$$

where WINDSG = time-varying wind velocity, meters/sec

A minimum value of 2 cm/hr is imposed on K20. Windspeed affects reaeration, then, above 6 meters/sec. The reaeration velocity used to compute volatilization is either the flow-induced reaeration or the wind-induced reaeration, whichever is larger.

7.9 APPLICATIONS

TOXIWASP was first used to study pesticide runoff into the upper Yazoo River, Mississippi (Mulkey et al., 1982). Predicted cumulative frequencies of pesticide concentrations were compared to those generated by HSPF (Johanson et al., 1980), by EXAMS, and by analytical solutions. TOXIWASP was used by Battelle Pacific Northwest Laboratories to estimate the consequences of pesticide leaching into canals in Florida (Mulkey, 1984). JRB, Inc. applied TOXIWASP to calculate the distribution of copper, nickel, and zinc in Deep River, North Carolina (Wagner, 1984). Model predictions were compared to data from two surveys. Metal concentrations were well correlated with observed toxicological effects on cerio-daphnia.

At present, TOXIWASP is being used by EPA's Integrated Environmental Management Program to calculate the upstream tidal transport of volatile organic chemicals from a wastewater effluent to a water supply intake in the Delaware Estuary. It also is being used by GKY, Inc. and Versar, Inc. in a regulatory impact study of the chemical industry in the Delaware Estuary.

7.10 TOXIWASP AVAILABILITY

To obtain the program TOXIWASP along with sample datasets and support software, write to:

Center for Water Quality Modeling
Environmental Research Laboratory
U.S. Environmental Protection Agency
College Station Road
Athens, GA 30613

Specify the computer system on which you will install the program. A nine-track magnetic tape will be mailed to you. Please copy the contents and return the tape.

Two source codes are contained on the magnetic tape. One runs on a DEC PDP mini computer with an IAS operating system and a 32K word user area. The other runs on an IBM mainframe with an OS/MVS operating system. Minor changes are required to install the program on other computers.

REFERENCES

Burns, L. A., D. M. Cline, and R. R. Lassiter. 1982. Exposure Analysis Modeling System (EXAMS): User Manual and System Documentation. U.S. Environmental Protection Agency, Athens, GA. EPA-600/3-82-023.

Covar, A. P. 1976. "Selecting the Proper Reaeration Coefficient for Use in Water Quality Models." Presented at the U.S. EPA Conference on Environmental Simulation and Modeling, April 19-22, 1976.

DiToro, D. M., J. J. Fitzpatrick, and R. V. Thomann. 1982. Water Quality Analysis Simulation Program (WASP) and Model Verification Program (MVP) - Documentation. Hydroscience, Inc., Westwood, NY, for U.S. Environmental Protection Agency, Duluth, MN, Contract No. 68-01-3872.

Feigner, K. D. and H. S. Harris. 1970. Documentation Report FWQA Dynamic Estuary Model. U.S. Dept. of the Interior, Federal Water Quality Administration, Washington, DC.

Huber, W. C., J. P. Heaney, M. A. Medina, W. A. Peltz, H. Sheikh, and G. F. Smith. 1974. Storm Water Management Model User's Manual, Version II, University of Florida, Gainesville, FL, for U.S. Environmental Protection Agency, Cincinnati, OH, EPA-670/2-75-017.

Johanson, R. C., J. C. Imhoff, and H. H. Davis, Jr. 1980. Users Manual for Hydrological Simulation Program--FORTRAN (HSPF). U.S. Environmental Protection Agency, Athens, GA. EPA-600/9-80-015.

Karickhoff, S. W., D. S. Brown, and T. A. Scott. 1979. Sorption of hydrophohic pollutants on natural sediments. Water Research, 13: 241-248.

Mackay, D. and P. J. Leinonen. 1975. Rate of evaporation of low solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol., 9:1178-1180.

Mill, T., W. R. Mabey, P. C. Bomberger, T. W. Chou, D. G. Hendry, and J. H. Smith. 1982. Laboratory Protocols for Evaluating the Fate of Organic Chemicals in Air and Water. U.S. Environmental Protection Agency, Athens, GA. EPA-600/3-82-0220.

Mulkey, L. A., personal communication, 1984.

Mulkey, L. A., R. B. Ambrose, and T. O. Barnwell, Jr. 1982. Aquatic Fate and Transport Modeling Techniques for Predicting Environmental Exposure to Organic Pesticides and Other Toxicants. International Workshop on the Comparison of Application of Mathematical Models for the Assessment of Changes in Water Quality in River Basins, both Surface and Groundwater, La Coruna, Spain.

Paris, D. F., D. L. Lewis, J. T. Barnett, and G. L. Baughman. 1975. Microbial Degradation and Accumulation of Pesticides in Aquatic System. U.S. Environmental Protection Agency, Washington, DC. EPA-660/3-75-007.

Rao, P. S. C. and J. M. Davidson. 1980. Estimation of Pesticide Retention and Transformation Parameters Required in Nonpoint Source Pollution Models. In: Environmental Impact of Nonpoint Source Pollution, M. R. Overcash and J. M. Davidson, Eds. Ann Arbor Science, Ann Arbor, MI. pp. 23-67.

Roesch, S. E., L. J. Clark, and M. M. Bray. 1979. User's Manual for the Dynamic (Potomac) Estuary Model. U.S. Envirnmental Protection Agency, Annapolis, MD, Technical Report 63, EPA 903/9-79-001.

Smith, J. H., W. R. Mabey, N. Bohonos, B. R. Holt, S. S. Lee, T-W. Chou, D. C. Bomberger, and T. Mill. 1977. Environmental Pathways of Selected Chemicals in Freshwater Systems. Part I: Background and Experimental Procedures. U.S. Environmental Protection Agency, Athens, GA. EPA-600/7-77-113.

Tsivoglou, E. E. and J. R. Wallace. 1972. Characterization of Stream Reaeration Capacity. U.S. Environmental Protection Agency, Washington, DC. EPA-R3-72-012.

Wagner, R., personal communication, 1984.

Wolfe, N. L., R. G. Zepp, G. L. Baughman, and J. A. Gordon. 1975. Kinetic investigation of malathion degradation in water. Bull. Environ. Contam. Toxicol., 13:707-713.

Wolfe, N. L., R. G. Zepp, G. L. Baughman, and D. M. Cline. 1977. Kinetics of chemical degradation of malathion in water. Environ. Sci. Technol., 11:88-93.

Zepp, R. G., N. L. Wolfe, J. A. Gordon, and G. L. Baughman. 1975. Dynamics of 2,4-D esters in surface waters: hydrolysis, photolysis, and vaporization. Environ. Sci. Technol., 9:144-150.

Zepp, R. G. and D. M. Cline. 1977. Rates of direct photolysis in aquatic environment. Environ. Sci. Technol., 11:359-366.

APPENDIX 1:
UNIT ABBREVIATIONS

°C	-	degrees Celcius
cm	-	centimeters
ft	-	feet
g	-	grams
hr	-	hours
kcal	-	kilocalories
kgb	-	kilograms biomass (dry weight)
kgs	-	kilograms sediment (dry weight)
L	-	length
loct	-	liters of octonol
l_w	-	liters of water in segment
l_T	-	liters total volume of segment
M	-	mass
$\underline{M}$	-	molarity, moles per liter
m	-	meters
MCF	-	million cubic feet total volume
MCF_w	-	million cubic feet of water in segment
mi	-	miles
mg	-	milligrams
mgb	-	milligrams biomass (dry weight)
mgc	-	milligrams chemical
mgs	-	milligrams sediment
ml	-	milliliters
n	-	moles chemical
sec	-	seconds
T	-	time
ug	-	micrograms
ugc	-	micrograms chemical